

UNITED STATES PATENT OFFICE

2,399,748

SIZING COMPOSITION FOR USE IN
PAPERMAKING

Andrew J. Luetzgen, Spring Grove, Pa., assignor,
by mesne assignments, to P. H. Glatfelter Com-
pany, Spring Grove, Pa., a corporation of Penn-
sylvania

No Drawing. Application March 9, 1943,
Serial No. 478,527

3 Claims. (Cl. 106—144)

This invention relates to sizing compositions for use in paper making. It provides a sizing material which is relatively low in cost, may be made from readily available materials, is particularly adapted for long storage or shipment prior to use, and forms a paper of high quality.

The sizing of paper is effected either by adding a sizing composition to the paper pulp in the beater before the pulp is formed into paper or by passing formed paper through a bath of sizing material. The latter operation is generally known as "tub-sizing" or "calender-sizing." The present invention is herein particularly described as applied to sizes intended for addition to the beater, but in certain circumstances it may be applicable to tub- or calender-sizing as well.

Various materials for the sizing of paper have heretofore been proposed. Generally speaking, paper sizes intended for use in the beater are added thereto in the form of emulsions and the sizing element is caused to deposit on the fiber by adding paper-makers' alum to the beater. The cost of the size and the cost of the alum both bulk large in the manufacturing expense.

Sizes have been proposed involving the use of clay and wax, and others have been proposed using rosin and clay; U. S. Patent to Walpuski, No. 313,263, U. S. Patent to Manson, No. 1,990,457. It has also been proposed to use a protective colloid, such as casein, in a size containing, e. g., rosin and clay; U. S. Patent to Grasshof et al., No. 2,271,691. These and like proposals have had several shortcomings. Sizes made according to the disclosures mentioned are unstable, a large part of the solids tending to separate out after a limited period of time, with the result that the sizes become either wholly unsatisfactory for use or else result in the production of an inferior grade of paper or are unsuited for long storage or for shipment over any considerable distance; or in their use cause "rosin specks" in the paper; or require the use of specially prepared clays of a colloidal nature; see, for example, the Manson and Grasshof et al. patents above mentioned. The Manson patent involves the use of colloidal clay. Such clays have a maximum particle size of the general order of $\frac{1}{2}$ micron. The Grasshof et al. patent employs electro-osmotically treated clay so as to attain a particle size of a diameter much less than 1 micron. Clays of the kinds just mentioned are relatively more expensive and less readily available than clays containing a substantial percentage of coarser particles.

My improved sizes, in contrast, may be made

very stable, give rise to no paper defects when intelligently used and may be made from clays less expensive and more readily available than those heretofore indicated. Moreover, my improved sizes are less expensive in themselves and may be precipitated in the beater with a small amount of alum or other acidifier, thus effecting a double saving.

I give below two specific examples of the making of my improved size. While these may be made in any suitable mixer, the examples here are for manufacture in a Bewoid mill, which I have found to be quite satisfactory for the purpose.

Example 1.—Rosin size

(a) Soak 12 lbs. of lactic casein in 9 gals. of water at 75–80° F. for about 5 minutes. Add 9½ oz. of caustic soda dissolved in a gallon of water to the casein and heat the mixture to about 100° F. with direct steam. This gives a total volume of casein solution of about 10 gals.

(b) From a rosin melting tank draw the equivalent of 430 lbs. of rosin into the mixer. Start the high-speed agitator at 280 to 300 R. P. M. and maintain a temperature of approximately 250° F. in the mixer.

(c) Add 6½ lbs. of caustic dissolved in 1 to 1½ gals. of water, taking care to add the caustic slowly enough to avoid excess foaming and splashing.

As the caustic solution is being added to the mixer, heat the casein solution to approximately 150° F. and at the same time heat water in an auxiliary vessel (35 gals. capacity is sufficient) to approximately 130° F.

(d) Add to the mixer 215 lbs. of either "Satin" or "Cosmic A" grade clay (hereinafter described) by running the mill at high speed and adding the clay as fast as good mixing permits.

The temperature of the mix at this point should not be above 220° F. If any difficulty is encountered in lowering the temperature to this figure, a thin stream of cold water may be directed into the mill while the clay is being added.

(e) Draw water from the auxiliary vessel and add it to the mix in sufficient quantity to reduce the temperature of the mix to 212° F. or slightly therebelow. It will be found that the mix thickens and the agitation becomes difficult. Then stir the casein solution into the mix. It will be found that the level of the mix will drop several inches on this addition. Now add water from the auxiliary vessel until the mix is away from the shaft and has a smooth appearance. The water should be added cautiously because better results

are obtained if the mixing is largely done while the size is most concentrated.

It will be found that a total of about 25 gals. of water is required in this step.

(f) Continue mixing at high speed for about 5 minutes.

At this stage the size has a concentration of about 70% solids. At room temperature it is a moderately viscous liquid which may be piped to or from tank cars or other containing vessels.

If the size is to be stored for any considerable length of time, a suitable preservative, e. g. formaldehyde (1 quart), should be added in the last stage of mixing.

The concentrated size may be added directly to the beater, or it may be extended with cold water before use. I have found it convenient to extend the size so that it can be metered through a gasoline measuring pump. This can be done with size previously made up, or it may be done as a final step of the manufacture. In this latter case, following step (f) above, I shift the Bewold mill to slow speed and then start adding water at a slow rate and at a temperature of about 85° F. The use of the slow speed avoids spilling over as this water is added. After about 8 gals. of water have been added, the rate at which it is added may be materially increased. The addition of water is continued until the desired percentage of solids has been added. I find that a size containing about 50% solids may be readily handled in a gasoline measuring pump.

Example 2.—Wax size

(a) Heat 210 lbs. of ordinary "scale wax" (unrefined paraffin of low melting point) to 200° F. in the mill and start the agitator at high speed. Add 105 lbs. of clay, such as "Satin" or "Cosmic A," and mix it thoroughly. The temperature at this point should be between 190 and 200° F.

(b) Add 25 lbs. of "Ammonia Soap 'C'" (from Harshaw Chemical Company of Cleveland, Ohio) and continue the mixing.

(c) In the meantime, allow 25 lbs. of lactic casein to swell in water and cut with 1½ lbs. of caustic soda at 120 to 140° F. Before adding the cut casein to the mix, heat the casein solution to 160–170° F. Add it rapidly to the mix, using high-speed agitation. The temperature at this point should be about 175° F.

(d) Add water at a temperature of 170 to 175° F. with high-speed mixing. The precise amount is gauged by appearance, water being added until the mix smooths out. This will ordinarily require from 2½ to 6 gals. As soon as the mix has smoothed out, stop adding water. Continue the high-speed agitation for about 5 minutes.

If the size is to be stored for a considerable period before using, add a preservative, e. g. a quart of formaldehyde, in the last stage of mixing.

In lieu of rosin or paraffin wax, other fusible binding agents such as other natural and synthetic resins and waxes other than paraffin may be used. This is a feature of importance because it permits of using materials most readily available at any particular time. Bituminous or petroleum distillate materials are generally unsuitable. Among other limitations, they are usually so strongly colored that they make the final paper color unsuitable for most purposes.

The initial addition of caustic in the rosin size (step b of Example 1 above) results in a saponification of a part of the rosin. Instead of proceeding in this fashion, it is permissible to re-

duce the quantity of rosin initially charged and add a rosin soap, thus paralleling steps a and b of Example 2 above. Ammonia Soap "C" is the reaction product of a fatty acid with ammonium hydroxide. Soaps other than Ammonia Soap "C" may be used. In any case, it is important in the manufacture of the size to form an admixture of the fusible binding agent and the clay with a compatible soap prior to the addition of the protective colloid. The mixing of the binding agent, the clay and the soap is effected at a temperature above the fusing point of the binding agent. Preferably, the protective colloid is added when the mix is at a temperature below that at which the major portion of the mixing is done. The procedure just outlined improves the quality of the size and, where saponification of rosin is effected in the mill, minimizes the possibility of impairment of the protective colloid, e. g., by hydrolysis.

Factors of my invention requiring detailed discussion are particle size and quantity of clay employed, concentration of the size and ratio between the amount of protective colloid used and the amount of alkali employed to "cut" it. By giving due regard to these factors, a size which remains stable over a long period of time and will yet go into solution readily, which is low in cost and which gives a high quality of paper may be obtained.

Particle size and quantity of clay employed.—The fact that the clays employed need not have particles of such minute dimensions as heretofore found necessary is a commercial important aspect of my invention. I have successfully used Georgia clays from the McIntyre district, produced by Edgar Brothers Company of Metuchen, New Jersey, and known commercially as their "Satin" and "Cosmic A" grades. "Satin" has particles as large as about 4 microns, some 5% of the clay by weight ranging down to 2 microns. "Cosmic A" is finer, but has particles as large as about 2.5 or 3 microns, some 8–10% of the clay by weight ranging down to 1 micron. These and similar clays are readily available in quantity in the United States, whereas, so far as I am aware, electro-osmotically separated clays are not available in this country, except possibly on a laboratory scale, and, if obtainable at all, are prohibitive in price.

My invention not only permits of using less expensive clays, but also of using a relatively higher ratio of clay to binding agent than heretofore. The clays which I am able to employ cost considerably less per ton than the fusible binding agents employed and it is therefore commercially advantageous to use a high percentage of clay in the size. My invention makes it possible to use clay in the amount of 50% of the weight of the binding agent, or even more provided that a sufficiently rugged mixer is available.

A size made according to my invention and containing clay as well as binding agent is equal or even superior in sizing effect, pound for pound, to a size having no clay; whereas no comparable cost advantage or quality advantage is obtained in the case of the expensive clays heretofore deemed necessary for use in paper sizes.

Concentration.—In order to permit of long storage or transport, it has heretofore been proposed that a clay-rosin size may be permitted to harden into a solid mass, and may later, for example, after long storage or after transport, be converted into a liquid dispersion with water

at elevated temperature; Grasshof et al. Patent 2,271,691. I have found that when dispersions are so formed, there is a marked increase in the tendency to form rosin specks in the paper. My sizing material, however, is an aqueous suspension so stable that it is unnecessary to reduce it to a solid mass for storage or shipment. Indeed, it should not be permitted even to have, in the fluid state, an unduly high concentration. The maximum permissible concentration is about 70% solids and for most purposes I prefer a concentration of about 65% solids. In concentrations greater than 70% the size proves exceedingly difficult to handle, particularly in cold weather, and if brought to the solid state it is very resistant to going into uniform suspension in water of any temperature sufficiently low to inhibit coalescence of the rosin.

I do not hazard any theory which would account for this difference between my size and those heretofore proposed. It may be due to the fact that I use coarser clays or to the difference in the order of manufacturing steps. At any rate, it indicates a marked difference in the character of the products.

At concentrations of 60-70% my size is remarkably stable and despite the fact that it contains clay particles ranging up to 2.5-3 or even 4 microns, it may be shipped, handled and stored over a period of months without losing the character of a substantially uniform viscous fluid free from agglomerations or sediment.

My size is readily receptive to the addition of a freezing-point depressant, such as ethylene glycol, which may be added if it is desired to protect the size against freezing in cold weather. If no depressant is added, the size will tend to separate if exposed to temperatures materially below 32° F.

Even if extended to a lesser concentration than 60-70%, the size remains stable for a considerable period of time. In the more dilute forms of the size there is some advantage in the use of "Cosmic A" clay over "Satin" clay. At a concentration of approximately 50% solids, a rosin size made with "Satin" or "Cosmic A" clay will remain stable for many weeks with no disadvantage except a slight separation of clay by sedimentation, the amount of sediment being somewhat greater with the use of "Satin" than with "Cosmic A," but in either case so small in amount that ample time is assured for extending the size in quantities for storage and use.

Ratio of protective colloid to alkali.—The stability of the size and its high quality in general will be diminished unless due precautions are taken in its manufacture to observe limiting ratios between the amount of protective colloid used and the amount of caustic employed to "cut" it.

The protective colloid which I prefer to use is casein, but I may use other proteins, e. g. albumen, vegetable proteins such as those derived from the soy bean, and gelatin. These proteins are effective protective colloids over a wide range of conditions, but in order to achieve my desired results the "cutting" of the colloid must be carefully controlled so that it neither forms aggregates of denatured protein or hydrolyzes. By way of specific example, as between lactic casein and caustic soda (on an anhydrous basis), the ratio by weight should be a minimum of about 20 casein to 1 of caustic; and a maximum of about 40 casein to 1 of caustic; that is to say, the caustic should not exceed about 5% of the weight of the

casein, or be less than about 2½%. Better results will be obtained with the higher figure. It will be found that the ratio will differ with different protein protective colloids, and vary somewhat depending on the amount of acid impurities in the colloid (casein), but in each case the principles to be observed are (a) that formation of aggregates of denatured protein, on the one hand, and hydrolysis, on the other, should be avoided, and (b) that one should approach (but not pass) that end of the range where hydrolysis occurs. A convenient rule is to use that amount of caustic which results in a cut colloid solution approximating maximum viscosity, other conditions being equal. If the amount of caustic required for imparting maximum viscosity to the casein solution is materially exceeded, there is a rapid diminution in viscosity which I believe to be due to hydrolysis of a substantial part of the casein.

In place of caustic soda other alkalis, for example caustic potash, or alkaline salts, for example soda ash, may be used to cut the casein, and I comprehend these by the term "alkaline cutting agent." In any case, the rule just stated remains applicable.

My invention makes it possible, by controlling the factors of particle size and of concentration, and by observing the principles herein stated as to the cutting of the protective colloid, to make a paper sizing composition which does not deteriorate and is remarkably stable. It is therefore admirably suited for being made up in quantity long in advance of use. This permits of it being made at a central point and shipped to the point of use. Freight costs are minimized because it is in concentrated form. On the other hand, no special difficulty will ordinarily be encountered in discharging it from the tank cars in which it is shipped, whereas sizes now on the market, such as rosin soap sizes, must be shipped in special cars and heated therein before it is possible to unload it. My improved size is readily mixable with water at room temperature and no difficulty is encountered in extending it either in the beater or preliminarily. It is thus admirably suited for quick use in the paper mill. My size is relatively low in cost. It is made from materials which are all available in adequate quantities and in such form that the raw material cost is low. As to the several ingredients used, the higher priced ones are in minimum quantity. The manufacturing cost is low and the shipping and storage costs are likewise low. The efficiency of the size, pound for pound, is higher than that of sizes heretofore employed so that a lesser quantity may be used. The alum requirements are correspondingly lessened, but the principal saving in alum is due to the fact that the alum requirements per pound are markedly low. The use of my improved size results in the production of paper of high quality, well sized and free from rosin specks.

I have described two present preferred embodiments of my invention. It will be understood, however, that these are by way of example only and that the invention may be otherwise embodied within the scope of the following claims.

I claim:

1. A sizing composition for use in paper making, in the form of an aqueous suspension and comprising a binding agent selected from the class consisting of the fusible resins and waxes, clay in the form of fine particles, there being particles as large as 2.5 microns, a compatible soap and a proteinaceous protective colloid, the colloid being cut with an alkaline cutting agent in the

amount of $2\frac{1}{2}$ to 5 per cent of the weight of the colloid so that hydrolysis of the colloid and formation of aggregates of denatured protein are inhibited, whereby the size of the individual particles in the sizing composition is uniformly small.

2. A sizing composition for use in paper making, in the form of an aqueous suspension and comprising a binding agent selected from the class consisting of the fusible resins and waxes, clay in the form of fine particles, there being particles as large as 2.5 microns, a compatible soap and casein cut with an alkaline cutting agent in the amount of $2\frac{1}{2}$ to 5 per cent of the weight of the casein,

whereby the size of the individual particles in the sizing composition is uniformly small.

3. A sizing composition for use in paper making, in the form of an aqueous suspension and comprising a binding agent selected from the class consisting of the fusible resins and waxes, clay in the form of fine particles, there being particles as large as 2.5 microns, a compatible soap and lactic casein cut with caustic soda in the amount of $2\frac{1}{2}$ to 5 per cent of the weight of the casein, whereby the size of the individual particles in the sizing composition is uniformly small.

ANDREW J. LUETTGEN.